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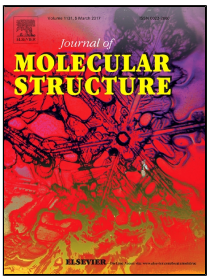

Synthesis of fluorescence organocyclotriphosphazene derivatives having functional groups such as formyl, Schiff base and both formyl and Schiff base without using Ar or N_2 atmosphere

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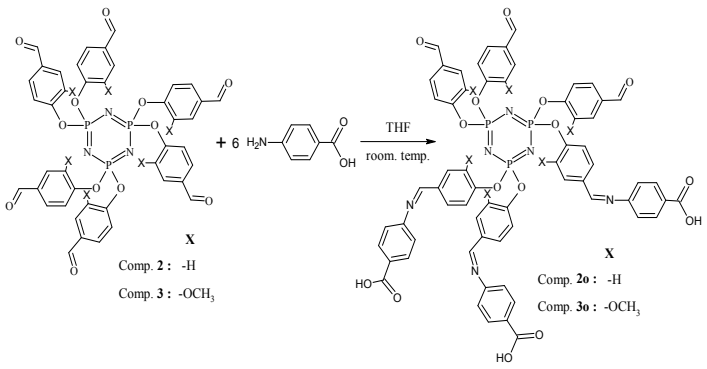

Organocyclotriphosphazenes bearing six formyl from hexachlorocyclotriphosphazene are generated in high yield without Ar or N_2 atmosphere. Organocyclotriphosphazenes involving six Schiff base groups do not occur from each of the aniline derivatives. The organocyclotriphosphazenes carrying both formyl and Schiff base units derivate from some aniline derivatives

Synthesis of fluorescence organocyclotriphosphazene derivatives having functional groups such as formyl, Schiff base and both formyl and Schiff base without using Ar or N_2 atmosphere

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Abstract

In the present study, hexa(4-formyl-phenoxy)cyclotriphosphazene(**2**) and hexa(4-formyl-2-methoxy-phenoxy)cyclotriphosphazene(**3**), which were previously synthesized in boiling solvent under N_2 atmosphere, were produced again at room conditions without using Ar or N_2 atmosphere by the same method. We detected that both **2** and **3** formed with very high yields even under this mild conditions. After that, 1 equiv of the compounds (**2** and **3**) were reacted with 12 equiv of some anilines derivatives with different substituted groups such as hydroxyl, cyano, mercapto, heterocyclic, carboxyl, chloro for the synthesis of new organocyclotriphosphazene derivatives incorporating six non-conjugated Schiff base groups. However, such compounds did not form from all of the selected anilines derivatives. The reactions of the compounds (**2** and **3**) with 4-carboxy-aniline and 4-cyano-aniline led to the formation of the organocyclotriphosphazenes bearing both formyl and Schiff base units. The structures of the synthesized molecules were determined using FT-IR, ^{1}H NMR and ^{31}P NMR. Then, the synthesized compounds were photophysically investigated by UV absorption and fluorescence emission spectroscopy in solution state. Photophysical studies indicate that the compound **1** and all of the obtained compounds have luminescence properties and large Stoke's shifts. Some compounds showed blue-red emission peak having rather large Stoke's shifts in the range of 390 to 800 nm.

Keywords: Cyclotriphosphazene, organophosphazene, phosphazene, Schiff base, fluorescence.

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1. Introduction

The production of organocyclotriphosphazenes from hexachlorocyclotriphosphazene has still continued to attracted great attention for several reasons since 1960. First, large number of organocyclotriphosphazene is possible to prepare from the reactions of hexachlorocyclotriphosphazene with various organic compounds such as alcohol, phenol, amine, thiol, Grignard or organolithium reagents [1-7]. But, the majority of the reported organocyclotriphosphazenes were synthesized from alcohol, phenol and amine derivatives. Second, these compounds have large potential applications in wide area such as chemistry, biochemistry and industry [8]. Third, these compounds are stable to air and water [9].

Among reported organocyclotriphosphazenes, there are relatively few studies related to the synthesis of organocyclotriphsopahazenes bearing functional groups like formyl, Schiff base, carboxyl acid, thiol, nitro, amino, hydroxyl, cyano, diazo or halogen in the literature. They are very important compounds for new organocyclotriphosphazenes derived from them. For example, different organocyclotriphosphazene derivatives carrying Schiff base, hydroxyl, carboxylic acid, ester or ether are generated from condensation, oxidation, reduction or substitution reaction of organocyclotriphosphazenes involving formyl groups. Until today, this type of compounds has been obtained from some formyl substituted phenol derivatives, such as 4-hydroxybenzaldehyde, 2-hydroxybenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-2-methoxybenzaldehyde, 5-chloro-2-hydroxybenzaldehyde and 5-bromo-2-hydroxybenzaldehyde in the literature [10-14]. Researchers prepare such organocyclotriphosphazenes by two different methods [15]. Both methods are performed under Ar or N_2 atmosphere. The preparation of organocyclotriphosphazenes from hexachlorocyclotriphosphazene is generally performed under Ar or N_2 atmosphere.

There have been relatively few reports on the synthesis of organocyclotriphosphazenes containing non-conjugated six Schiff base moieties from organocyclotriphosphazene bearing formyl groups [11, 14, 16-18]. Especially, the organocyclotriphosphazenes containing both formyl and Schiff base groups are not available in the literature. The Schiff bases with one or two imine groups without phosphazene generally reported in the literature. There are relatively few works about

the synthesis of conjugated Schiff base macrocyclic containing six or more than six imines [19, 20].

In recent years, fluorescence properties of the synthesized compounds in chemistry have been extensively studied [21]. Less research has been reported on the luminescence of the organophosphazenes, even though many organophosphazenes have been prepared. The luminescence and the synthesis of Schiff base compounds are much better known and more studied than organocyclotriphosphazenes. Our group has previously synthesized new organocyclotriphosphazenes carrying six formyl and six Schiff base groups In addition, we determined the fluorescence properties of these compounds [11, 14].

Herein, without using Ar or N_2 atmosphere, we firstly synthesized the organocyclotriphosphazenes bearing six formyl groups from hexachlorocylotriphosphazene in the presence of K_2CO_3 at room temperature. Some new organocyclotriphosphazenes bearing six non-conjugated Schiff base moieties were derived from the reactions of the organocyclotriphosphazenes bearing formyl groups with aniline and some aniline derivatives. However, we detected surprisingly that the organocyclotriphosphazenes bearing both formyl and Schiff bases groups derived from 1 equiv of organocyclotriphosphazenes bearing six formyl groups and 12 equiv of 4-cyano-aniline and 4-carboxyl-aniline. Luminescence has been investigated at room temperature in THF solution. Some derived organocyclotriphosphazenes are blue-red luminescent compound.

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene ($N_3P_3Cl_6$), 4-hydroxybenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde, 4-methoxy-benzylamine, aniline and aniline derivatives were purchased from Aldrich and used as received. Acetonitrile and THF which used as solvent in the reactions were purchased from Merck and used without further purification. All the reactions were carried out at room conditions without N_2 or Ar atmosphere.

2.2. Instrumentation

NMR spectra were obtained on a Varian Mercury 400 MHz. Infrared spectra were recorded on a Perkin Elmer Spectrum Two spectrometer with ATR in the region of 4000−400 cm^{-1}. Electronic absorption and fluorescence spectra in solution were recorded by Shimadzu mini 1240 UV spectrophotometer and Shimadzu RF-1501 spectrofluorometer, respectively. The melting points were measured on a Electrothermal IA 9200 apparatus in capillary.

2.3. Synthesis

2.3.1. Hexa(4-formyl-phenoxy)cyclotriphosphazene (2). 4-hydroxybenzaldehyde (17.56 g, 103.55 mmol) was added to a mixture of $N_3P_3Cl_6$ (1) (3.00 g, 8.63 mmol) and K_2CO_3 (14.40 g, 103.55 mmol) in acetonitrile (300 mL) at room conditions. The reaction was stirred for 24 h at room temperature. After acetonitrile used as solvent was removed under vacuum, CH_2Cl_2 (350 mL) was poured into the residual solid. The mixture was filtered and the solvent was evaporated to about 30 mL. Then solution of the mixture was slowly added to ethanol (400 mL) and a white solid precipitated out. The resulting white solid was filtered, washed with hexane and dried at room temperature. The yield of the compound **2** was 6.02 g (81%): mp:157 ºC. FT-IR (cm^{-1}): 1704 (HC=O), 1206, 1180 and 1156 (P=N), 960 (P-O-Aryl). ^{1}H NMR δ (ppm, $(CD_3)_2CO$): 10.0 (H-C=O), 8.0-7.0 (Aryl H). ^{31}P NMR δ (ppm): 7.95.

2.3.2. General procedure for synthesis of the compounds 2a-2o from the compound 2. A solution of the compound **2** (0.50 g, 0.580 mmol) and primary amine derivatives (6.960 mmol) in THF (50 mL) was stirred for 24 h at room temperature. THF was removed under vacuum. After CH_2Cl_2 (5 mL) was poured into the residual mixture, the solution was slowly added to ethanol (80 mL) and a solid precipitated out. The resulting solid was filtered, washed with hexane and then dried at room temperature. (The name of the color of the compounds was mentioned in the web site: http://en.wikipedia.org.)

2.3.2.1. Hexa[4-(phenyliminomethyl)phenoxy]cyclotriphosphazene (2a). The compound **2a** was prepared from aniline (0.64 mL, 6.960 mmol) as a beige color solid according to general procedure. Yield: 0.52 g (68%): mp:175 ºC. FTIR (cm^{-1}): 1626 (HC=N), 1199, 1181, 1171, 1156 (P=N), 958 cm^{-1}(P-O-Aryl). ^{1}H NMR δ (ppm, $CDCl_3$): 8.24 (H-C=N), 7.62-6.93 (Aryl H). ^{31}P NMR δ (ppm): 7.93.

2.3.2.2. Hexa[4-(1-naphthyliminomethyl)phenoxy]cyclotriphosphazene (2b). The compound **2b** was prepared from 1-naphthylamine (0.997 g, 6.960 mmol) as a straw color solid according to general procedure. Yield: 0.80 g (85%): mp:155 ºC. FTIR (cm^{-1}): 1626 (HC=N), 1201, 1181, 1177, 1156 (P=N), 957 (P-O-Aryl). ^{1}H NMR δ (ppm, $CDCl_3$): 8.64 ppm (H-C=N), 8.45-7.00 (Aryl H). ^{31}P NMR δ (ppm): 8.70.

2.3.2.3. Hexa[4-(3,4-bischloro-phenyliminomethyl)phenoxy]cyclotriphosphazene (2c). The compound **2c** was prepared from 3,4-dichloroaniline (1.128 g, 6.960 mmol) as a cream color solid according to general procedure. Yield: 0.80 g (80%): mp:193 ºC. FTIR (cm^{-1}): 1626 (HC=N), 1201, 1178, 1155 (P=N), 950 (P-O-Aryl). The NMR analysis of the compound was not performed because insoluble in any solvent, such as $(CD_3)_2CO$, $CDCl_3$, DMSO-D.

2.3.2.4. Hexa[4-(2-mercapto-phenyliminomethyl)phenoxy]cyclotriphosphazene (2d). The compound **2d** was prepared from 2-mercapto-aniline (0.75 mL, 6.960 mmol) as a peach color solid according to general procedure. Yield: 0.60 g (69%): mp: 133 ºC. FTIR (cm^{-1}): 1602 (HC=N), 1202, 1178, 1160 (P=N), 951 (P-O-Aryl). ^{1}H NMR δ (ppm, $(CD_3)_2SO$): 8.00-6.00 ppm (protons peaks for imine, thiol, and aromatic protons), 3.45 (H_2O), 2.40 ($(CH_3)_2SO$). ^{31}P NMR δ (ppm):8.75.

2.3.2.5.Hexa[4-(2-mercapto-benzimidazol-5-yl-iminomethyl)phenoxy] cyclotriphosphazene (2e). The compound **2e** was prepared from 5-amino-2-mercaptobenzimidazole (1.150 g, 6.960 mmol) as a selective yellow color solid according to general procedure. Yield: 0.55 g (55%): mp: 310 ºC. FTIR (cm^{-1}): 3119 cm^{-1}(N-H), 1635 (C=N), 1626 (HC=N), 1199, 1177, 1161 (P=N), 953 (P-O-Aryl). ^{1}H NMR δ (ppm, $(CD_3)_2SO$): 12.6 and 12.0 (N-H ve S-H), 8.55 (H-C=N) 7.8-6.3 (the protons peaks for aromatic), 3.45 (H_2O), 2.40 ($(CH_3)_2SO$). ^{31}P NMR δ (ppm): 8.25.

2.3.2.6. Hexa[4-(1H-indazol-6-yl-iminomethyl)phenoxy]cyclotriphosphazene (2f). The compound **2f** was prepared from 6-amino-1H-indazole (0.928 g, 6.960 mmol) as a apricot color solid according to general procedure. Yield: 0.78 g (87%): mp:170 ºC. FTIR (cm^{-1}): 3231 (OH), 1629 (HC=N), 1200, 1178, 1157 (P=N),943 (P-O-Aryl). The NMR analysis of the compound was not performed because insoluble in any solvent, such as $(CD_3)_2CO$, $CDCl_3$, DMSO-D.

2.3.2.7. Hexa[4-(fluoren-2-yl-iminomethyl)phenoxy]cyclotriphosphazene (2g). The compound **2g** was prepared from 2-aminofluorene (1.261 g, 6.960 mmol) as a sunset color solid according to general procedure. Yield: 0.77 g (72%): mp:302 ºC. FTIR (cm^{-}

^{1}): 1627 (HC=N), 1205, 1175, 1157 (P=N), 961 (P-O-Aryl). The NMR analysis of the compound was not performed because insoluble in any solvent, such as $(CD_3)_2CO$, $CDCl_3$, DMSO-D.

2.3.2.8. Hexa[4-(2-hydroxy-phenyliminomethyl)phenoxy]cyclotriphosphazene (2h). The compound **2h** was prepared from 2-hydroxy-aniline (0.760 g, 6.960 mmol) as a naples yellow color solid according to general procedure. Yield: 0.64 g (78%): mp:154 ºC. FTIR (cm^{-1}): 3414 (O-H), 1625 (HC=N), 1202, 1177 and 1158 (P=N), 955 (P-O-Aryl). ^{1}H NMR δ (ppm, $CDCl_3$): 8.77 (H-C=N), 8.00-6.80(Aryl H). ^{31}P NMR δ (ppm): 8.66.

2.3.2.9.Hexa[4-(5-chloro-2-hydroxy-phenyliminomethyl)phenoxy] cyclotriphosphazene (2i). The compound **2i** was prepared from 5-chloro-2-hydroxy-aniline (0.999 g, 6.960 mmol) as a naples yellow color solid according to general procedure. Yield: 0.5 g (53%): mp:160 ºC. FTIR (cm^{-1}):3421 (O-H), 1624 (HC=N), 1206, 1174 and 1158 (P=N), 957 (P-O-Aryl). ^{1}H NMR δ (ppm, $CDCl_3$): 8.76 (H-C=N), 8.00-6.80 (Aryl H). ^{31}P NMR δ (ppm): 8.66.

3.3.2.10.Hexa[4-(4-hydroxy-phenyliminomethyl)phenoxy]cyclotriphosphazene (2j). The compound **2j** was prepared from 4-hydroxy-aniline (0.760 g, 6.960 mmol) as a peach yellow color solid according to general procedure. Yield: 0.80 g (97%): mp: 185 ºC. FTIR (cm^{-1}): 3414 (O-H), 1623 (HC=N), 1205, 1178, 1159 (P=N), 959 (P-O-Aryl). ^{1}H NMR δ (ppm, $CDCl_3$): 8.55 (H-C=N), 7.80-6.50 (Aryl H). ^{31}P NMR δ (ppm): 9.14.

2.3.2.11.Hexa[4-(4-mercapto-phenyliminomethyl)phenoxy]cyclotriphosphazene (2k). The compound **2k** was prepared from 4-mercapto-aniline (0.871 g, 6.960 mmol) as a peach yellow color solid according to general procedure. Yield: 0.74 g (85%): mp:330 ºC. FTIR (cm^{-1}): 1624 (HC=N), 1190, 1178, 1158 (P=N), 953 cm^{-1}(P-O-Aryl). The NMR analysis of the compound was not performed because insoluble in any solvent, such as $(CD_3)_2CO$, $CDCl_3$, DMSO-D.

2.3.2.12. Hexa[4-(4-methoxy-benzyliminomethyl)phenoxy]cyclotriphosphazene (2l). The compound **2l** was prepared from 4-methoxy-benzylamine (0.91 mL, 6.96 mmol) as a white color solid according to general procedure. Yield: 0.80 g (88%): mp:88 ºC. FTIR (cm^{-1}): 1640 (HC=N), 1204, 1172, 1156 (P=N), 952 cm^{-1}(P-O-Aryl). ^{1}H NMR δ (ppm, $CDCl_3$): 8.33 (H-C=N), 7.70-6.80 (Aryl H), 4.69 (-CH_2-), 3.77 (CH_3O-). ^{31}P NMR δ (ppm): 8.89.

2.3.2.13. Hexa[4-(isoquinolin-5-yl-iminomethyl)phenoxy]cyclotriphosphazene (2m). The compound **2m** was prepared from 5-aminoisoquinoline (1.00 g, 6.960 mmol) as a atomic trangerine color solid according to general procedure. Yield: 1.0 g (100%): mp:145 ºC. FTIR (cm^{-1}): 1625 (HC=N), 1198, 1176, 1155 (P=N), 953 (P-O-Aryl). ^{1}H NMR δ (ppm, $CDCl_3$): 9.3 (H-C=N for 5-amino-isoquoniline), 8.67 (H-C=N), 8.53-7.20 (the peaks of aromatic protons). ^{31}P NMR δ (ppm): 8.62.

2.3.2.14. 6,6-di(4-(4-cyano-phenyliminomethyl)phenoxy)-2,2,4,4-tetra(4-formyl-phenoxy)cyclotriphosphaze (2n). The compound **2n** was prepared from 4-cyano-aniline (0.820 g, 6.960 mmol) as a white color solid according to general procedure. Yield: 0.50 g (80%): mp: 115 ºC. FTIR (cm^{-1}): 2225 (C≡N), 1699 (HC=O), 1630 (HC=N), 1200, 1176, 1157 (P=N), 953 (P-O-Aryl). ^{1}H NMR δ (ppm, $CDCl_3$): 9.98(H-C=O, integral area:100), 8.58 (H-C=N, integral area:38.68), 8.00-6.80 (Aryl H). ^{31}P NMR δ (ppm): 8.20-7.70 (multiple).

2.3.2.15. 2,2,4-tri(4-(4-carboxy-phenyliminomethyl)phenoxy)-4,6,6-tri(4-formyl-phenoxy)cyclotriphosphazene (2o). The compound **2o** was prepared from 4-carboxy-aniline (0.954 g, 6.960 mmol) as a white color solid according to general procedure. Yield: 0.5 g (70%): mp:357 ºC. FTIR (cm^{-1}): 1683 (HOC=O and HC=O), 1631 (HC=N), 1202, 1175, 1159 cm^{-1} (P=N), 953 cm^{-1}(P-O-Aryl). ^{1}H NMR δ (ppm, DMSO): 12.35 (-COOH), 9.88 (H-C=O, integral area: 98.73), 8.52 (H-C=N, integral area:100), 8.00-6.00 (Aryl H). ^{31}P NMR δ (ppm): 8.38-7.58 (multiple).

2.3.3. Hexa(4-formyl-2-methoxy-phenoxy)cyclotriphosphazene (3). 4-hydroxy-3-methoxy-benzaldehyde (vanilline) (15.76 g, 103.55 mmol) was added to a mixture of $N_3P_3Cl_6$ (1) (3.00 g, 8.63 mmol) and K_2CO_3 (14.40 g, 103.55 mmol) in acetonitrile (300 mL) at room conditions. The reaction was stirred for 24 h at room temperature. After acetonitrile was removed under vacuum, CH_2Cl_2 (350 mL) was poured into the residual solid. The mixture was filtered and the solvent was evaporated to about 30 mL. Then solution of the mixture was slowly added to ethanol (400 mL) and a white solid precipitated out. The resulting white solid was filtered, washed with hexane and dried at room temperature. The yield of the compound **3** was 6.74 g (75%): mp: 182 ºC. FTIR (cm^{-1}): 1692 (HC=O), 1186, 1147, 1116 (P=N), 947 (P-O-Aryl). ^{1}H NMR δ (ppm, $(CD_3)_2SO$): 9.40 (H-C=O), 7.20-7.60 (Aryl H), 3.80 (H_3CO-). ^{31}P NMR δ (ppm): 8.00.

2.3.4. General Procedure for synthesis of the compounds 3a-3o from the compound 3. A solution of the compound **3** (0.4 g, 0.384 mmol) and primary amine derivatives

(4.608 mmol) in THF (50 mL) was stirred for 24 h at room temperature. THF was removed under vacuum. After CH_2Cl_2 (5 mL) was poured into the residual mixture, the solution was slowly added to ethanol (80 mL) and a solid precipitated out. The resulting solid was filtered, washed with hexane and then dried at room temperature. (The name of the color of the compounds was mentioned in the web site: http://en.wikipedia.org.)

2.3.4.1. Hexa[2-methoxy-4-(phenyliminomethyl)phenoxy]cyclotriphosphazene (3a). The compound **3a** was prepared from aniline (0.42 mL, 4.608 mmol) as a champagne solid according to general procedure. Yield: 0.37 g (64%): mp: 109 ºC. FTIR (cm^{-1}): 1627 (HC=N), 1215, 1181, 1147 (P=N), 949 (P-O-Aryl). ^1H NMR δ (ppm, $(CD_3)_2SO$): 8.49 (H-C=N), 7.60-7.20 (Aryl H), 3.98 (H_3CO-). ^{31}P NMR δ (ppm): 9.14.

2.3.4.2. Hexa[2-methoxy-4-(1-naphthyliminomethyl)phenoxy]cyclotriphosphazene (3b). The compound **3b** was prepared from 1-naphthylamine (0.660 g, 4.608 mmol) as a buff solid according to general procedure. Yield: 69% (0.81 g), mp.:134 ºC. FTIR (cm^{-1}): 1625 (HC=N), 1185, 1155 (P=N), 950 (P-O-Aryl). ^1H NMR δ (ppm, $(CD_3)_2SO$): 8.60 (H-C=N), 8.35-7.00 (Aryl H), 3.98 (H_3CO-). ^{31}P NMR δ (ppm): 9.14.

2.3.4.3.Hexa[2-methoxy-4-(3,4-bischloro-pheyliminomethyl)phenoxy] cyclotriphosphazene (3c). The compound **3c** was prepared from 3,4-dichloro-aniline (0.747 g, 4.608 mmol) as a jasmine solid according to general procedure. Yield: 0.76 g (100%): mp.:115 ºC. FTIR (cm^{-1}): 1627 (HC=N), 1184, 1150 (P=N), 949 (P-O-Aryl). ^1H NMR δ (ppm, $(CD_3)_2SO$): 8.28 (H-C=N), 7.60-7.20 (the peaks of aromatic protons), 3.97 (H_3CO-). ^{31}P NMR δ (ppm): 9.00.

2.3.4.4.Hexa[2-methoxy-4-(2-mercapto-pheyliminomethyl)phenoxy] cyclotriphosphazene (3d). The compound **3d** was prepared from 2-mercapto-aniline (0.50 mL, 4.608 mmol) as a peache-orange solid according to general procedure. Yield: 0.60 g (91%): mp:120 ºC. FTIR (cm^{-1}): 1624 (HC=N), 1199, 1181, 1171, 1156 (P=N), 957 (P-O-Aryl). ^1H NMR δ (ppm, $(CD_3)_2SO$): 8.40 (HC=N), 7.78-6.30 (the peaks of aromatic protons), 5.37 (H-S-), 3.98 (H_3CO-). ^{31}P NMR δ (ppm): 8.50.

2.3.4.5.Hexa[2-methoxy-4-(2-mercapto-benzimidazol-5-yl-iminomethyl)phenoxy] cyclotriphosphazene (3e). The compound **3e** was prepared from 5-amino-2-mercaptobenzimidazole (0.761 g, 4.608 mmol) as a pumpkin solid according to general procedure. Yield: 1g (100%): mp.:280 ºC. FTIR (cm-1): 1636 (C=N), 1613 (HC=N), 1186, 1158, 1114 (P=N), 953cm-1(P-O-Aryl). 1H NMR δ (ppm, (CD3)2SO): 12.5 (N-H

and SH), 8.55 (H-C=N), 7.5-7.0 (the peaks of aromatic protons), 3.80 (H3CO-). 31P NMR δ (ppm): 8.54.

2.3.4.6.Hexa[2-methoxy-4-(1H-indazol-6-yl-iminomethyl)phenoxy] cyclotriphosphazene (3f). The compound **3f** was prepared from 5-amino-1H-indazole (0.614 g, 4.608 mmol) as an apricot solid according to general procedure. Yield: 0.78 g (54%): mp:195 ºC. FTIR (cm^{-1}): 1636 (HC=N), 1625 (HC=N), 1187, 1154, 1119 (P=N), 943 (P-O-Aryl). The NMR analysis of the compound was not performed because insoluble in any solvent, such as $(CD_3)_2CO$, $CDCl_3$, DMSO-D.

2.3.4.7.Hexa[2-methoxy-4-(fluoren-2-yl-iminomethyl)phenoxy] cyclotriphosphazene (3g). The compound **3g** was prepared from 2-aminofluorene (0.835 g, 4.608 mmol) as a tangerine solid according to general procedure. Yield: 0.77 g (97%): mp.:112 ºC. FTIR (cm^{-1}): 1626 (HC=N), 1183, 1150 (P=N), 950 (P-O-Aryl). ^1H NMR δ (ppm, $(CD_3)_2SO$): 8.56 (HC=N), 7.7-7.0 (the peaks of aromatic protons), 3.97 (H_3CO-), 3.60 (-H_2C-). ^{31}P NMR δ (ppm): 8.99.

2.3.4.8.Hexa[2-methoxy-4-(2-hydroxy-phenyliminomethyl)phenoxy] cyclotriphosphazene (3h). The compound **3h** was prepared from 2-hydroxy-aniline (0.503 g, 4.608 mmol) as a pumpkin solid according to general procedure. Yield: 0.78 g (85%) mp: 142 ºC. FTIR (cm^{-1}): 3425 (-O-H), 1625 (HC=N), 1190, 1177 and 1152 (P=N), 952 cm^{-1}(P-O-Aryl). ^1H NMR δ (ppm, $CDCl_3$): 8.80 (H-C=N), 7.90-6.50 (Aryl H), 3.65 (CH_3O-). ^{31}P NMR δ (ppm): 8.88.

2.3.4.9.Hexa[2-methoxy-4-(5-chloro-2-hydroxy-phenyliminomethyl)phenoxy] cyclotriphosphazene (3i). The compound **3i** was prepared from 5-chloro-2-hydroxy-aniline (0.662 g, 4.608 mmol) as a peach yellow solid according to general procedure. Yield: 0.68 g (79%): mp:115 ºC. FTIR (cm^{-1}): 3345 (-O-H), 1625 (HC=N), 1190, 1168 and 1151 (P=N), 954 cm^{-1}(P-O-Aryl). ^1H NMR δ (ppm, $CDCl_3$): 8.80 (H-C=N), 7.90-6.50 (Aryl H), 3.94 (CH_3O-). ^{31}P NMR δ (ppm): 8.87.

2.3.4.10.Hexa[2-methoxy-4-(4-hydroxy-phenyliminomethyl)phenoxy] cyclotriphosphazene (3j). The compound **3j** was prepared from 4-hydroxy-aniline (0.503 g, 4.608 mmol) as a peach yellow solid according to general procedure. Yield: 0.78 g (85%): mp: 185 ºC. FTIR (cm^{-1}): 1623 (HC=N), 1191, 1180, 1148 (P=N), 954 cm^{-1}(P-O-Aryl). ^1H NMR δ (ppm, $CDCl_3$): 8.49 (H-C=N), 7.60-6.60 (Aryl H), 3.89 (CH_3O-). ^{31}P NMR δ (ppm): 9.38.

2.3.4.11.Hexa[2-methoxy-4-(4-mercapto-phenyliminomethyl)phenoxy] cyclotriphosphazene (3k). The compound **3k** was prepared from 4-mercapto-aniline (0.577 g, 4.608 mmol) as an amber solid according to general procedure. Yield: 0.64 g (%65): mp:218 ºC. FTIR (cm^{-1}): 1618 (HC=N), 1188, 1180, 1151 (P=N), 953 cm^{-1}(P-O-Aryl). The NMR analysis of the compound was not performed because insoluble in any solvent, such as $(CD_3)_2CO$, $CDCl_3$, DMSO-D.

2.3.4.12.Hexa[2-methoxy-4-(4-methoxy-benzyliminomethyl)phenoxy] cyclotriphosphazene (3l). The compound **3l** was prepared from 4-methoxy-benzylamine (0.60 mL, 4.608 mmol) as a white solid according to general procedure. Yield: 0.65 g (54%): mp:105 ºC. FTIR (cm^{-1}): 1643 (HC=N), 1181, 1150, 1119 (P=N), 947 cm^{-1}(P-O-Aryl). ^{1}H NMR δ (ppm, $CDCl_3$): 8.31 (H-C=N), 7.40-6.60 (Aryl H), 4.69 (-CH_2-), 3.65 (CH_3O-). ^{31}P NMR δ (ppm): 9.00.

2.3.4.13.Hexa[2-methoxy-4-(isoquinolin-5-yl-iminomethyl)phenoxy] cyclotriphosphazene (3m). The compound **3m** was prepared from 5-aminoisoquinoline (0.664 g, 4.608 mmol) as an atomic tangerine solid according to general procedure. Yield: 0.74 g (85%): mp:138 ºC. FTIR (cm^{-1}): 1624 (HC=N), 1186, 1163, 1148 (P=N), 950 (P-O-Aryl). ^{1}H NMR δ (ppm, $CDCl_3$): 9.19 (HC=N for 5-aminoisoquoniline), 8.30 (HC=N), 8.5-7.0 (the peaks of aromatic protons), 3.94 (H_3CO-). ^{31}P NMR δ (ppm): 8.54.

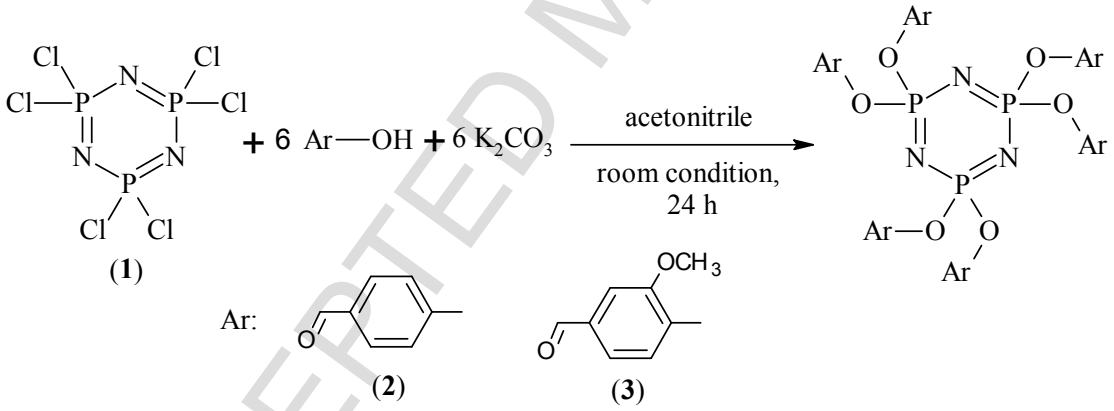
2.3.4.14. 2,2,4,4-tetra(2-methoxy-4-(4-cyano-phenyliminomethyl)phenoxy)-6,6-tri(2-methoxy-4-(4-cyano-phenyliminomethyl)phenoxy)cyclotriphosphazene (3n). The compound **3n** was prepared from 4-cyano-aniline (0.544 g, 4.608 mmol) as a white solid according to general procedure. Yield: 0.5 g (60%): mp:115 ºC. FTIR (cm^{-1}): 2225 (C≡N), 1699 (HC=O), 1630 (HC=N), 1200, 1176, 1157 (P=N), 953 (P-O-Aryl). ^{1}H NMR δ (ppm, $CDCl_3$): 9.98(H-C=O, integral area:180.93), 8.58 (H-C=N, integral area:372.82), 8.00-6.80 (Aryl H), 3.98 (H_3CO-). ^{31}P NMR δ (ppm): 8.20-7.70 (multiple).

2.3.4.15.2,2,4-tri(2-methoxy-4-(4-carboxy-phenyliminomethyl)phenoxy)-4,6,6-tri(2-methoxy-4-formyl-phenoxy)cyclotriphosphazene (3o). The compound **3o** was prepared from 4-carboxy-aniline (0.632 g, 4.608 mmol) as a white solid according to general procedure. Yield: 0.57 g (70%): mp:357 ºC. FTIR (cm^{-1}): 1683 (HOC=O), 1631 (HC=N), 1202, 1175, 1159 cm^{-1} (P=N), 953 cm^{-1}(P-O-Aryl). ^{1}H NMR δ (ppm, DMSO):

12.40 (-COOH) 9.86 (H-C=O, integral area:100), 8.49 (H-C=N, integral area:110), 8.00-6.50 (Aryl H), 3.80 (CH_3O-). ^{31}P NMR δ (ppm): 8.38-7.58 (multiple).

3. Results and Discussion

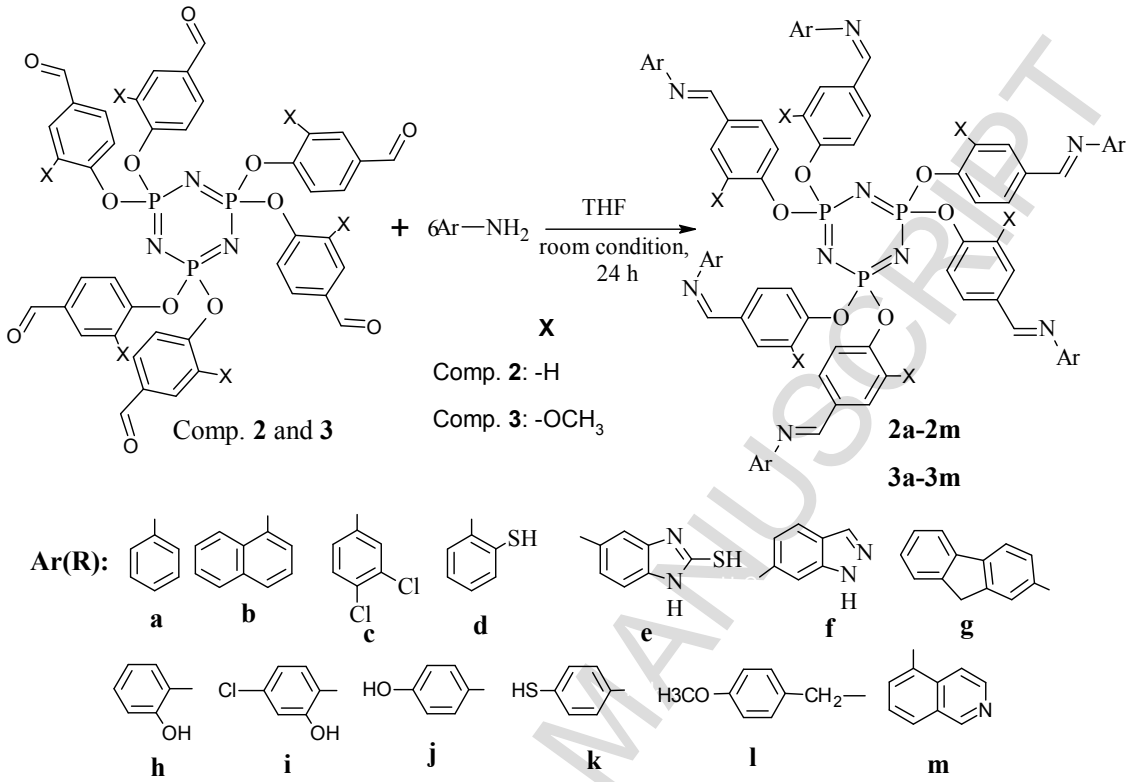
Carriedo et al. and Tümer et al. reported firstly that hexa(4-formyl-phenoxy)cyclotriphosphazene(**2**) and hexa(4-formyl-2-methoxy-phenoxy)cyclotriphosphazene(**3**) were derived with 91% and 74% yields in refluxing solvent under N_2 atmosphere, respectively [10,12]. In the present study, the compounds **2** and **3** were obtained again with 81% and 75% yields at room temperature without using Ar or N_2 atmosphere according to Schemes 1. These compounds were prepared via the reactions of hexachlorocyclotriphosphazene (**1**) with 12 equiv of 4-formyl-phenol and 4-formyl-2-hydroxy-phenol in the presence of K_2CO_3 (12 equiv**).** Both **2** and **3** were successfully purified by precipitation method which is the easiest and the most economical. In addition, the reagents and solvents used in the reactions were not purified before we used. When these reactions are carried out under N_2 atmosphere or without using Ar or N_2 atmosphere, the compounds **2** and **3** forms in very high yields.



Scheme 1. Structure and synthesis route for the compounds **2** and **3**

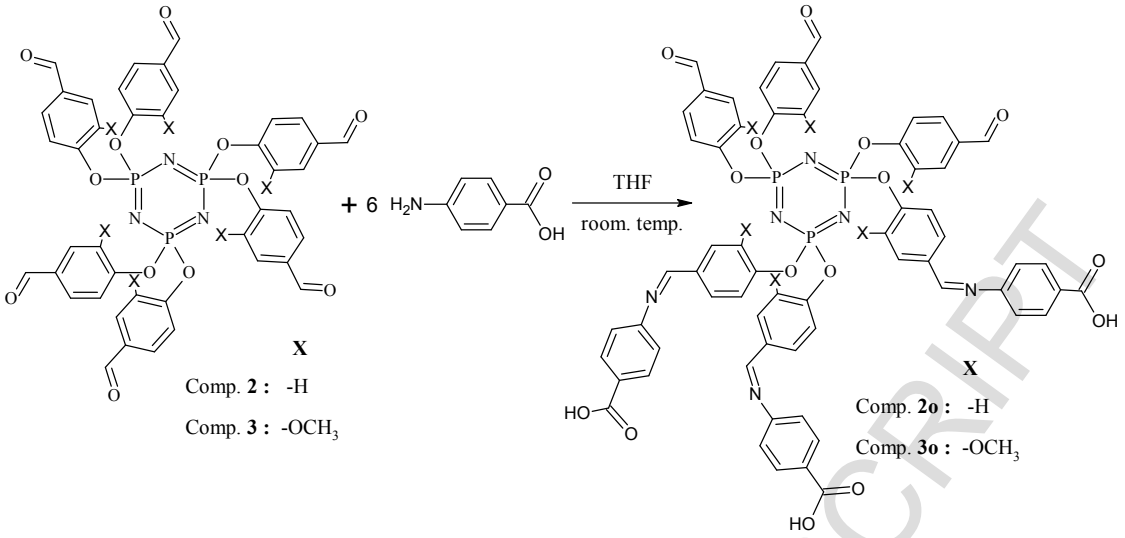
An equivalent of the compounds **2** and **3** were treated with 12 equivalent of some primary amines for the obtained of organocyclotriphosphazene derivatives containing six Schiff base groups. Selected primary amines are aniline (**a**), 1-naphthylamine (**b**), 3,4-dichloroaniline (**c**), 2-mercapto-aniline (**d**), 5-amino-2-mercapto-1H-benzimidazole (**e**), 5-amino-1H-indazole (**f**), 2-aminofluorene (**g**), 2-hydroxy-aniline (**h**), 5-chloro-2-hydroxy-aniline (**i**), 4-hydroxy-aniline (**j**), 4-mercapto-aniline (**k**), 4-methoxy-benzylamine (**l**), 5-aminoisoquinoline (**m**), 4-cyano-aniline (**n**) and 4-carboxyaniline (**o**). We determined that the organocyclotriphosphazenes bearing six Schiff base

moieties derived from aniline (**a**), 4-methoxy-benzylamine (**l**) and some aniline derivatives (**b-m**), expect for 4-cyano-aniline (**n**) and 4-carboxyaniline (**o**) (**Scheme 2**).

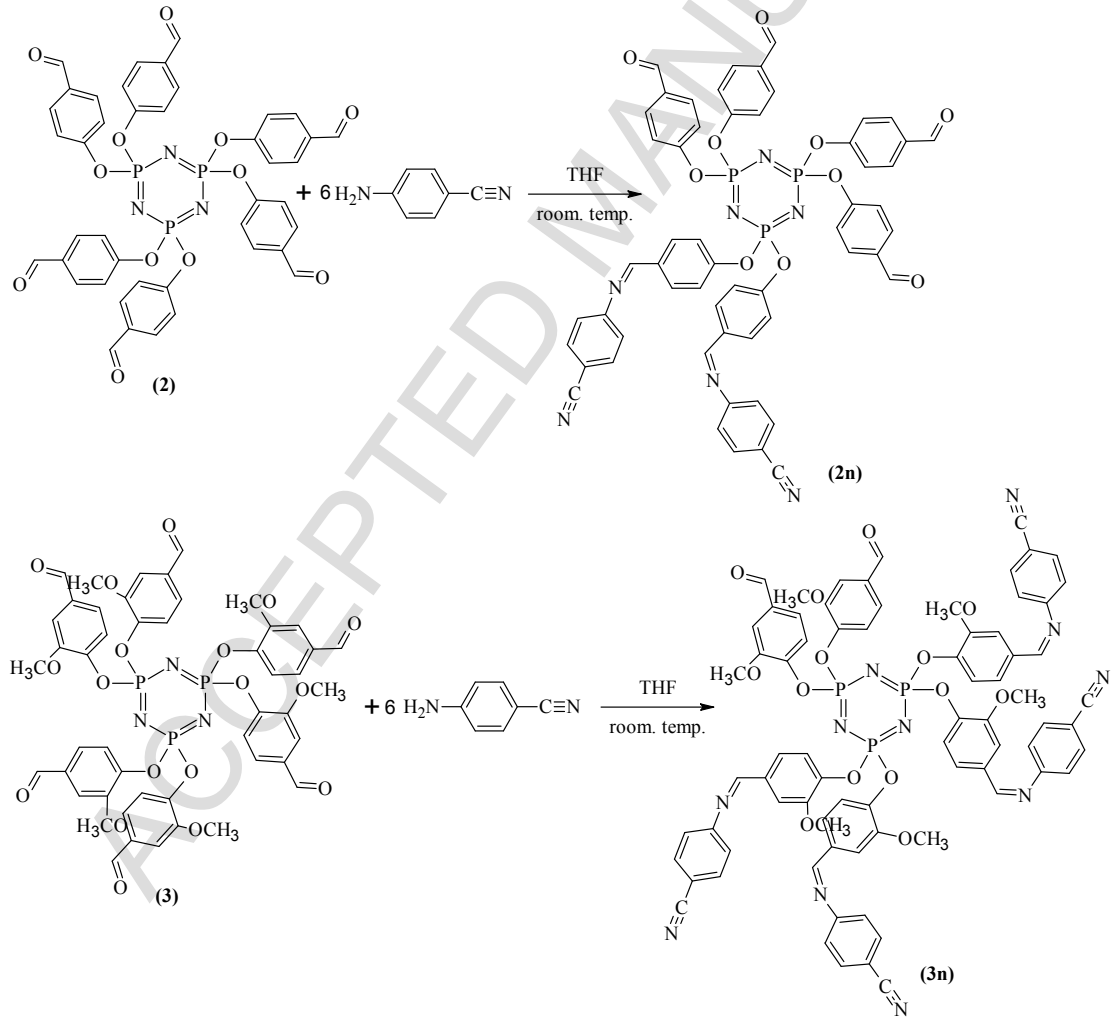


Scheme 2. Structure and synthetic route for the organocyclotriphosphazenes with six imine groups

The reactions of both **2** and **3** with these two aniline derivatives led to the formation of the organocyclotriphosphazenes carrying both formyl and Schiff base moieties (**Scheme 3, 4**). On para position of 4-cyano-aniline (**n**) and 4-carboxyaniline (**o**) have electron-withdrawing group such as -CN, -COOH.



Scheme 3. Structure and synthetic route for the organocyclotriphopshazenes carrying both imine and formyl groups from *p*-carboxy-aniline



Scheme 4. Structure and synthetic route for the organocyclotriphopshazenes(**2n** and **3n**) carrying both imine and formyl groups from *p*-cyano-aniline

While the organocyclotriphosphazenes (**2o** and **3o**) bearing the same number of formyl and Schiff base groups occur from the reactions of both the compound **2** and the compound **3** with 4-carboxyaniline (**o**), the organocyclotriphosphazenes (**2n** and **3n**) bearing different number of formyl and Schiff base moieties consist from 4-cyano-aniline (**n**). The structures of all the prepared compounds were confirmed using FT-IR, ^{1}H NMR, and ^{31}P NMR.

The FT-IR spectra of all the synthesized compounds (**2**, **3**, **2a-2o** and **3a-3o**) exhibit characteristic strong bands in the range of 1220-1150 cm^{-1} and 980-940 cm^{-1}, which can be assigned to -P=N− and P-O-Aryl, respectively. These bands confirm distinctly the presence of phosphazene and phenoxy bounded of phosphazene ring. In the IR spectra of the compounds (**2**, **3**), the strong peak observed at 1703 and 1695 cm^{-1} were attributed to the presence of aldehyde groups. But, in the IR spectra of the compounds (**2a-2m**, **3a-3m**) which have six imine groups, no peak was found at 1705-1680 cm^{-1} illustrating the presence of the carbonyl group. Imine (C=N) stretching vibrations in the spectra of these compounds appear in the range of 1645–1610 cm^{-1}. As shown in the **Fig. 1** and **Fig. 2**, the peaks at 1705-1680 cm^{-1} and 1645–1610 cm^{-1} in the spectra of the compounds (**2n-2o**, **3n-3o**) proved the existence of both Schiff base and formyl units. The IR spectra of organocyclotriphosphazenes bearing Schiff base moieties showed no signals due to the $-NH_2$.

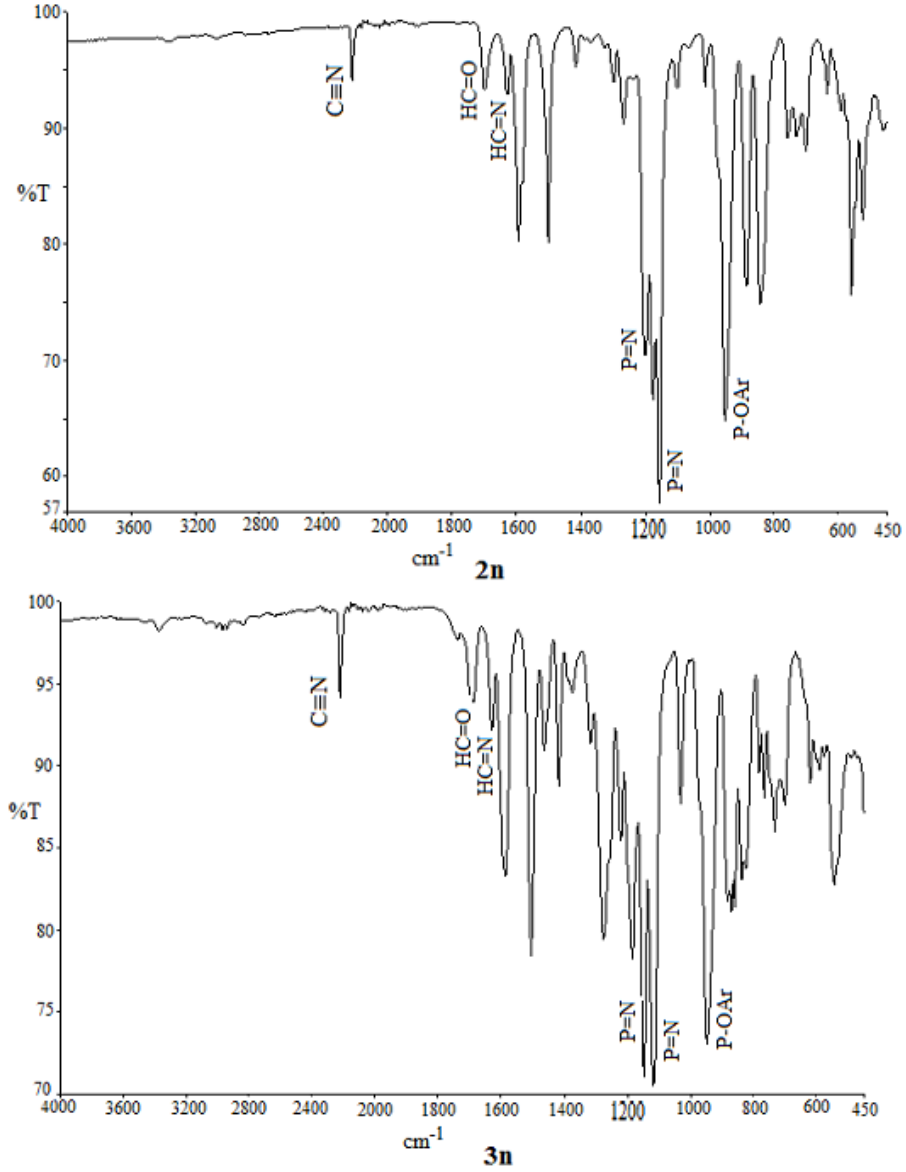


Fig. 1. FTIR spectra of the compounds **2n** and **3n**

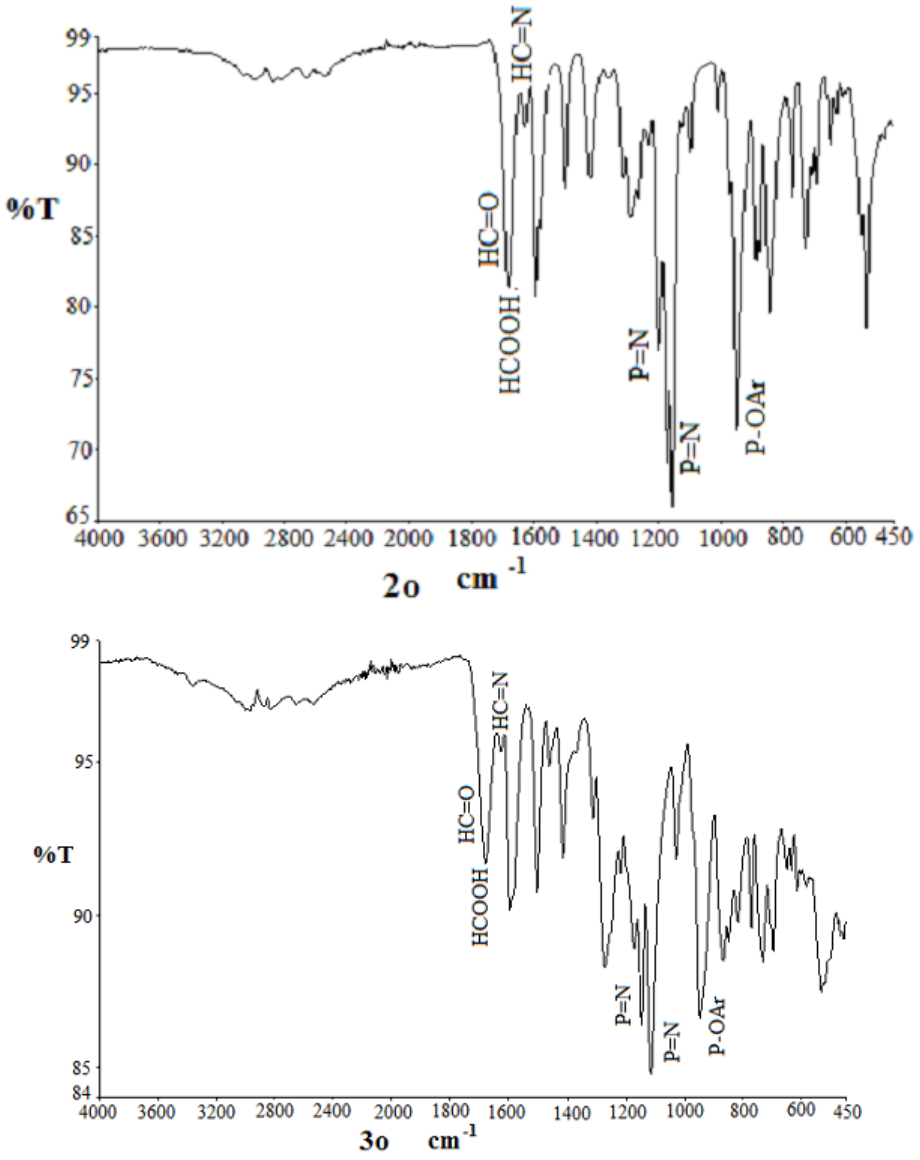


Fig. 2. FTIR spectra of the compounds **2o** and **3o**

The ^{1}H and ^{31}P NMR data of all the compounds were given in experimental section. All these spectral analyses confirm the proposed structure of all the compounds. ^{1}H NMR spectra of the compounds **2** and **3** show a peak at around 10.0 ppm, belonging to the aldehyde proton. However, this aldehyde proton peak disappears in organocyclotriphosphazenes derivatives containing six Schiff base groups (**2a-2m**, **3a-3m).** The imine proton for the compounds was observed at about 8.30 ppm as singlet in the spectra. The methoxy protons attached to the phenoxy ring was observed at about 3.80 ppm in the spectra of the compounds **3** and its derivatives. Two peaks corresponding to formyl proton at about 10.0 ppm (HC=O) and imine proton at 8,30 ppm(HC=N) were present in the ^{1}H NMR spectra of organocyclotriphosphazenes

carrying both formyl and Schiff base moieties (**2n-3n**, **20-3o)** (**Fig. 3** and **Fig. 4**). According to the integral areas supplied by ^{1}H NMR data, the molar ratios of the two functional groups were calculated. While the molar ratios of formyl to imine were indeed 1:1(integral area ratio:100:98.73) and 1:1 (integral area ratio:110:100) for **2o** and **3o**, the molar ratios are 4:2 (integral area ratio:100:38.68) and 2:4 (integral area ratio:180.93:372.82) for **2n** and **3n,** respectively. As in the FT-IR spectra, the signal due to the -NH_2 protons relating to primary amine were not appears in the region 5.0 ppm in the ^{1}H NMR spectra.

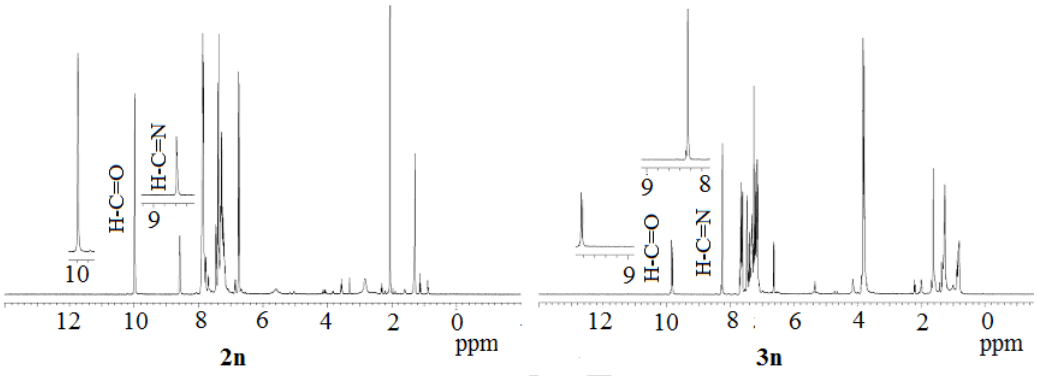


Fig. 3. ^{1}H NMR spectra of the compounds **2n** and **3n**

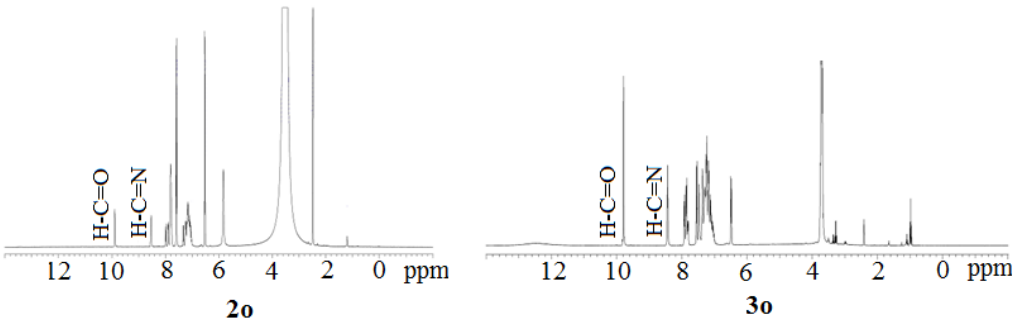


Fig. 4. ^{1}H NMR spectra of the compounds **2o** and **3o**

The proton-decoupled ^{31}P NMR spectra of the compounds (**2**, **3**, **2a-2m**and **3a-3m)** exhibit A_3 type spin systems due to same phosphors environments within the molecule as expected. The signal of all the phosphor atoms in these compounds was observed in the range of 9.0-6.0 ppm as single. But, the signal of the phosphorus atoms in the compounds (**2n, 2o**, **3n, 3o)** was observed in the range of 8.50-7.50 ppm as multiple (**Fig. 5** and **Fig. 6**). Because the multiple peaks were observed very small chemical shift (1 ppm), the chemical environment of the phosphorus is not determined from ^{31}P NMR spectra.

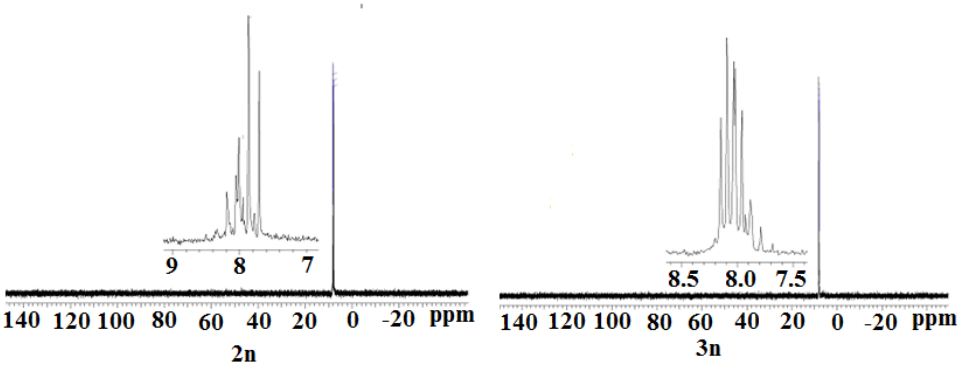


Fig. 5. ^{31}P NMR spectra of the compounds **2n** and **3n**

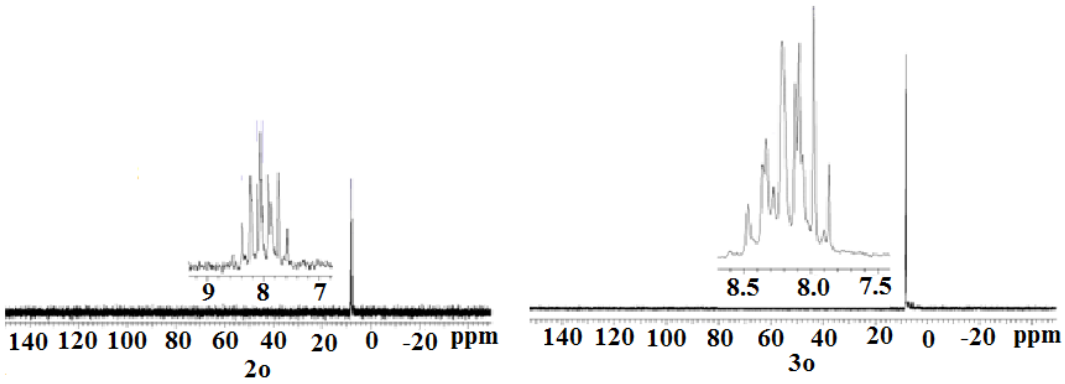


Fig. 6. ^{31}P NMR spectra of the compounds **2o** and **3o**

UV–vis absorption and photoluminescence spectra of the compound **1** and all the synthesized compounds were recorded in THF medium in the range 200–900 nm. Table 1 and Table 2 summarize UV–Vis, excitation and maximum fluorescence wavelengths of all the compounds. The UV–vis absorption spectra of organocyclotriphosphazene derivatives shows absorption wavelengths between 220 nm and 360 nm assigned to the $\pi \rightarrow \pi^*$ transitions. The absorption spectra for the compounds **2** and **3** presented two peaks. Allcock reported that the UV-vis. spectrum of the compound **1** exhibited only one absorption bands at 175 nm [9]. But, we observed one peak at 287 nm (log∑:3) in the UV-vis. spectrum of the compound **1** in THF.

Fluorescence spectra of the compound **1** and the prepared compounds show emission peak. Therefore, the compound **1** and the prepared compounds are fluorescence. The excitation wavelengths were detected at 220-350 nm for all the compounds. While emission peak of the compounds **2** and **3** show in the ultraviolet region, the majority of the compounds derived from the compounds **2** and **3** exhibited

emission peak in the visible region. Among all the compounds, the compounds **1, 2j** and **3g** are the most fluorescence compounds. They have shown intense emission band at 608, 745 and 753 nm and the largest Stoke's shift. The emission values of some organocyclotriphospahazene obtained from the same aniline derivatives are quite different.

4. Conclusions

At the end of this study, we have achieved very interesting results. The organocyclotriphosphazenes involving six formyl groups were obtained in very high yield from hexachlorocyclotriphosphazene and formyl substituted phenols derivatives in the presence of K_2CO_3 at room temperature without Ar or N_2 atmosphere. The reactions of these compounds with aniline derivatives cause to the formation of organocyclotriphosphazenes bearing non-conjugated six Schiff base units. However, organocyclotriphosphazenes bearing non-conjugated six Schiff base units are not prepared from all of the aniline derivatives. If there is an electron withdrawing group on aniline derivatives, like cyano, carboxyl, organocyclotriphosphazenes containing both formyl and Schiff base units derive from theirs. Furthermore, organocyclotriphosphazenes bearing non-conjugated six Schiff base units are also produce from aniline derivatives carrying heterocyclic group. Organocylotriphosphazenes are fluorescent compounds. Many of organocyclotriphosphazenes containing formyl or Schiff base groups can exhibit fluorescence emission peak in visible region. Such phosphazenes have the potential to be used as fluorescence.

Acknowledgements

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Table 1. Photophysical and Stoke's Shift data of the compounds **1, 2** and **2a-2o**

Comp.	Cons. (mol/L)	Absorption $\lambda_{max.}$, nm (logε)	Excitation, $\lambda_{Ex.}$, nm (logε)	Emission $\lambda_{Em.}$, nm (logε)	Stoke's Shift $\Delta\lambda_{ST}$ (nm)
1	$8.63x10^{-5}$	175(4.0)[a], 287(3)	**268(7.0)**	**608(6.0)**	**340**
2	$3.87x10^{-5}$	250(4.8), 329(3.2)	307(7.5)	341(7.5)	34
2a	$3.60x10^{-5}$	238(4.7), 259(4.9), 290(4.8), 315(4.7)	**307(7.3)**	**400(7.3)**	**93**
2b	$2.27x10^{-5}$	239(5.0), 257(5.0), 290(4.9), 349(4.8)	285(7.0)	331(7.3)	46
2c	$2.51x10^{-5}$	241(4.9), 263(5.0), 290(5.0), 316(5.0)	**307(7.5)**	**401(7.5)**	**94**
2d[c]	$3.10x10^{-5}$	241(4.9), 271(4.8), 297(5.0), 307(5.0)	**267(7.5)**	**401(7.5)**	**134**
2e[c]	$2.10x10^{-5}$	269(5.0), 325(4.9)	336(7.7)	374(7.7)	38
2f[b]	-	-	-	-	-
2g[b]	-	-	-	-	-
2h	$2.37x10^{-5}$	241(4.8), 265(5.0), 288(5.0), 352(5.0)	**308(7.5)**	**407(7.6)**	**99**
2i	$2.27x10^{-5}$	241(4.9), 265(4.9), 287(4.9), 360(4.8)	238(7.1)	330(7.0)	92
2j	$2.37x10^{-5}$	242(4.9), 269(4.7), 285(4.7), 329(4.7)	**309(7.3)**	**745(7.4)**	**436**
2k[b]	-	-	-	-	-
2l	$2.75x10^{-5}$	251(5.0)	307(7.6)	339(7.5)	32
2m	$2.68x10^{-5}$	236(*4.92*), 264(*4.95*), 287(*4.88*), 342(*4.65*)	**262(7.6)**	**436(7.6)**	174
2n	$3.45x10^{-5}$	260(4.9), 292(4.9)	255(7.3)	351(7.2)	96
2o[c]	$3.83x10^{-5}$	239(4.2), 284(4.5)	326(7.4)	355(7.4)	29

[a][9]

[b] Optical properties of the compound could not be analyzed because of insoluble in any solvent.

[c] The spectra were recorded in DMSO

Table 2. Photophysical and Stoke's Shift data of the compounds **3** and **3a-3o**

Comp.	Cons. (mol/L)	Absorption $\lambda_{max.}$, nm (logε)	Excitation, $\lambda_{Ex.}$, nm (logε)	Emission $\lambda_{Em.}$, nm (logε)	Stoke's Shift $\Delta\lambda_{ST}$
3	$3.20x10^{-5}$	258(4.9), 304(4.6)	240(7.5)	336(7.5)	96
3a	$2.90x10^{-5}$	238(4.8), 264(4.9), 287(4.9), 315(50)	**246(7.4),**	**398(7.4)**	**134**
3b	$1.90x10^{-5}$	240(5.1), 262(5), 294(5.0), 315(5.0), 343(4.9)	285(6.9)	338(6.5)	53
3c	$2.27x10^{-5}$	240(4.9), 269(4.9), 290(4.9), 324(5.1)	**250(7.5)**	**401(7.5)**	**151**
3d[c]	$2.37x10^{-5}$	241(5.0), 267(4.9), 287(4.9), 315(4.9)	**304(7.5)**	**406(7.6)**	**102**
3e[c]	$1.73x10^{-5}$	270(5.2), 322(5.1), 360(5.2)	**336(7.0)**	**413(7.0)**	**77**
3f[b]	-	-	-	-	-
3g	$1.65x10^{-5}$	239(5.0), 289(4.9), 356(4.8)	**300(7.6)**	**753(7.6)**	**453**
3h	$2.31x10^{-5}$	238(4.9), 271(4.9), 286(4.9), 350(4.9)	293(7.1)	328(7.1)	55
3i	$1.67x10^{-5}$	239(5.0), 289(4.9), 356(4.8)	**254(7.8)**	**409(7.8)**	**155**
3j	$1.88x10^{-5}$	239(5.0), 274((4.8), 330(4.9)	264(7.5)	305(7.5)	41
3k[b]	-	-	-	-	-
3l	$1.90x10^{-5}$	258(4.9), 296(4.6)	**245(7.6)**	**399(7.6)**	**154**
3m	$2.04x10^{-5}$	239(5.0), 269(4.8), 286(4.8), 322(4.9), 342(4.9)	**332(7.6)**	**512(7.7)**	**180**
3n	$2.54x10^{-5}$	242(5.0), 262(5.0), 294(5.1), 309(5.1)	294(7.6)	366(7.7)	72
3o[c]	$2.62x10^{-5}$	276(5.1), 291(5.1), 340(4.8)	324(7.6)	338(7.5)	14

[b] Optical properties of the compound could not be analyzed because of insoluble in any solvent.

[c] The spectra were recorded in DMSO